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**CRYOSORPTION OF HYDROGEN BY
12-20°K CARBON DIOXIDE CRYODEPOSITS**



R. Dawbarn

ARO, Inc.

July 1967

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FOREWORD

The research presented herein was sponsored by Arnold Engineering Development Center (AEDC), Air Force Systems Command (AFSC), Arnold Air Force Station, Tennessee, under Program Element 65402234.

The results of research reported herein were obtained by ARO, Inc. (a subsidiary of Sverdrup & Parcel and Associates, Inc.), contract operator of AEDC under Contract AF 40(600)-1200. The research was conducted in the Aerospace Environmental Facility (AEF) (AEDC) under ARO Project No. SW2705, and the manuscript was submitted for publication on May 22, 1967.

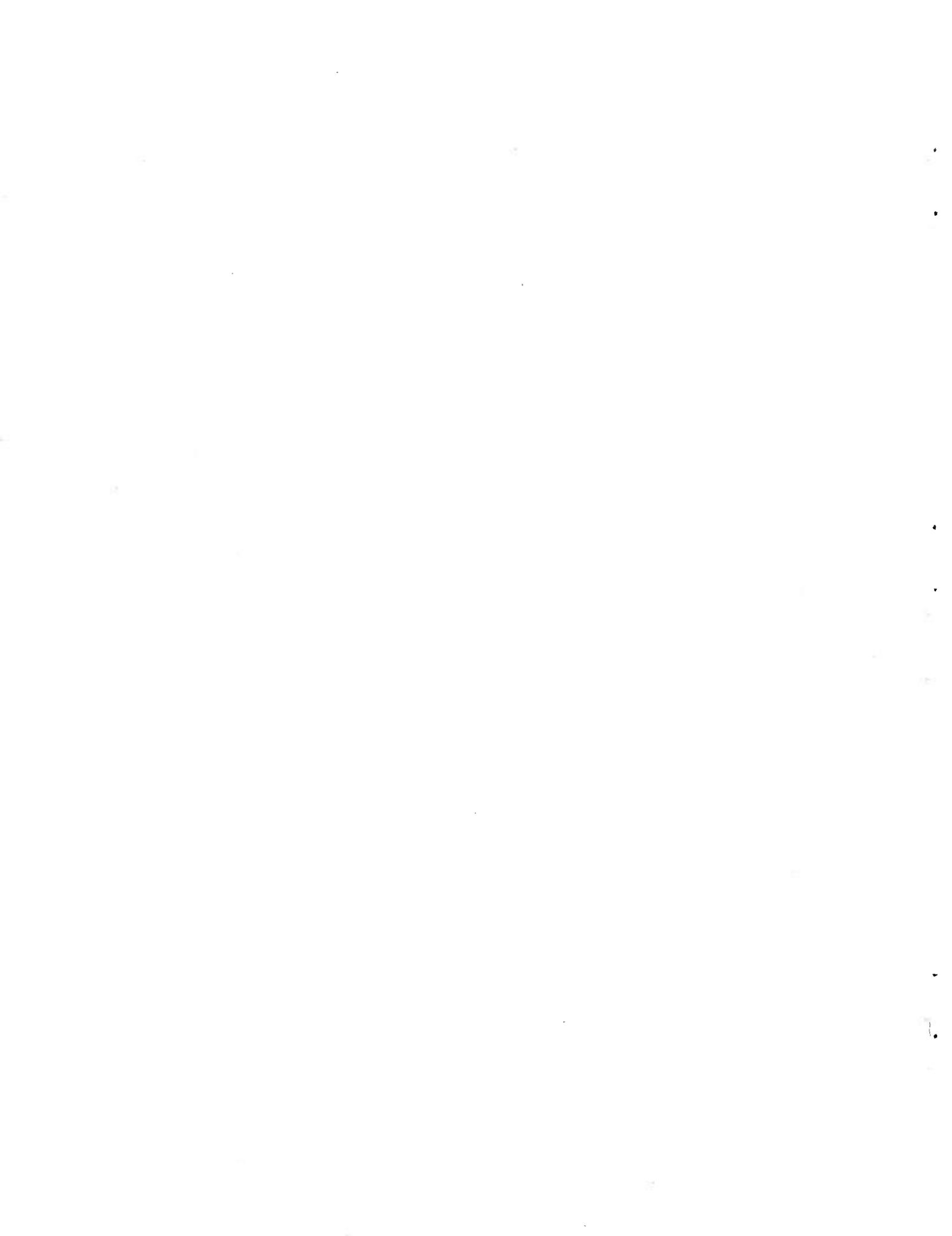
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ABSTRACT

Carbon dioxide cryodeposits were investigated to determine their ability to sorb H₂. Various thicknesses from 5×10^{-5} to 1×10^{-3} cm were used, at temperatures of 12, 16, and 20°K. Pumping speeds of 28, 19, and 14 l/sec-cm² were measured for the respective temperatures. An arbitrary "capacity" of the CO₂ cryodeposit for H₂ was defined. Within the limits of the experimental parameters varied, this capacity was found to be a direct function of the thickness of the cryodeposit and increased logarithmically as the temperature was lowered. No cryopumping of H₂ was observed with cryodeposits above 25°K. The CO₂ cryodeposits were readily contaminated by N₂, and the H₂ pumping speed dropped when N₂ was flowed in simultaneously with the H₂.



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NOMENCLATURE

K	Conductance of orifice in shroud, l/sec
k	Conductance of leak, l/sec
P	Pressure, mm Hg
R	Universal gas constant, $ergs/mole-^{\circ}K$
S	Pumping speed, l/sec
T	Temperature, $^{\circ}K$
t	Time, sec
V	Volume, l
ξ	Outgassing rate, l/sec
σ	Gage calibration factor, mm Hg/division

SUBSCRIPTS

c	Inside shroud inside vacuum chamber
f	Gas addition system
ms	Mass spectrometer
n	Gage scale
o	Outside shroud but inside vacuum chamber

SECTION I INTRODUCTION

Of the available methods of producing a vacuum environment, cryopumping offers the most promising means of producing a clean vacuum with exceptionally high pumping speeds. Unlike conventional cold trapped diffusion pumps, cryopumping is not limited by the conductance of the orifice leading to the pump. Since cryopanel can be built within the vacuum cell, their size is limited only by the size of the chamber and the quantity of cryogenic refrigerant available. The common atmospheric gases (N_2 , O_2 , CO_2 , H_2O , A) are condensable on 20°K surfaces with vapor pressures below 10^{-11} mm. Hydrogen (H_2) and helium (He), although not major constituents of the atmosphere, are used extensively in aerospace technology.

Frequently, it is necessary to remove one or both of these noncondensable gases from a vacuum chamber with a system having a high pumping speed, while still maintaining a clean vacuum. If the liquid-helium (LHe)-cooled panels are available, H_2 may be cryopumped directly since its vapor pressure is about 10^{-7} torr at 4.2°K. Super-cooled He has been used by Chubb et al. to improve pumping speed and reduce the base pressure still further (Ref. 1).

Helium cannot be practically cryopumped since cryosurfaces on the order of 0.4°K are required for vapor pressures of 10^{-7} torr. However, some work has been done in this laboratory investigating the feasibility of pumping He by sorption on cryodeposits of A, N_2 , and O_2 . Although there was no measurable pumping above 5°K, pumping speeds as high as 50 percent of the theoretical maximum were obtained at 4.2°K (Ref. 2).

In many instances, LHe is not available or not feasible in the quantities required to pump large systems. However, many large aerospace chambers have GHe refrigerators capable of operating relatively large cryoarrays in the temperature range from 12 to 20°K. Several methods of sorbing H_2 have been found, although efforts to find sorbents among molecular sieves and cryodeposits that would provide a practical method of pumping He in this temperature range have so far been unsuccessful. Southerlan (Ref. 3) reports successful pumping of H_2 by H_2O cryodeposits at 20°K. Busol and Yuferov present data for CO_2 cryodeposits at 20°K and suggest that acetone, gasoline, and alcohol condensed at 20°K will also sorb H_2 but not as effectively as CO_2 (Ref. 4). Using O_2 and N_2 as cryodeposits at 20°K, Hemstreet et al. found no significant pumping of H_2 ; however, they report favorably on Molecular Sieve #5A cooled to 20°K (Ref. 5).

The experiments reported herein were centered on the ability of CO₂ cryodeposits to sorb H₂. The three questions to be investigated were: (1) the effect of thickness of the CO₂ cryodeposit, (2) the effect of temperature of the CO₂, and (3) the results of the CO₂-coated cryo-panel pumping a mixture of H₂ and N₂.

SECTION II APPARATUS

The chamber used in this study is shown in Fig. 1. It consists essentially of a 36-in. -high by 30-in. -diam vacuum chamber containing a 7-in. -diam spherical cryosurface and two independent gas addition systems. The vacuum chamber is constructed of stainless steel, all heliarc welded. A 25-in. -high by 24-in. -diam inner shroud of 1/8-in. copper can be cooled by circulating LN₂ through tubing welded to its outer surfaces. The cryosphere is centrally located inside the shroud, and its fill and vent lines are vacuum jacketed and shielded inside the chamber. The surface area of the sphere, available for pumping, is 970 cm².

There are two gas addition systems, one to add H₂ and the other to add CO₂. The gas addition systems (Fig. 2) are similar, each consisting of a surge tank, a pressure gage for measuring the fore-pressure of the gas, and a series of sintered stainless steel leaks arranged in parallel (Ref. 6). Gas flows from 5×10^{-2} to 5×10^{-7} torr-ℓ/sec can be metered into the chamber. Each gas addition system has an independent pumping station.

A thin-walled circular orifice in the bottom of the shroud provides a convenient method for frequent in-place calibration of the gages and mass spectrometer (see Section IV). The pressure in the working volume of the chamber is monitored by an ion gage and a mass spectrometer. Tubulation inside the chamber prevents the gages from directly sensing either the cryosurface or the calibration orifice. The time constant of the tubulation is calculated as 3.8×10^{-6} sec for H₂ at 300°K, and thus the response is much faster than any pressure changes to be followed in these experiments. A second ion gage, located on the outside wall of the chamber, is used to read the pressure on the far side of the orifice.

The vacuum chamber pumping system consists of a 6-in. oil diffusion pump with a LN₂ baffle. The diffusion pump is backed by a mechanical roughing pump. The chamber can be isolated from the

pumping system by a 6-in. high vacuum, gate valve. The entire vacuum system is equipped with outgassing heaters capable of producing chamber temperatures up to 500°K.

The cryosphere was plumbed directly to a He refrigerator (180-w cryostat), via vacuum jacketed transfer lines. An adjustable needle valve, located in the cryostat, was used to set the GHe flow. Temperatures in the sphere were indicated by a H₂ vapor pressure thermometer centered in the cryosphere.

SECTION III PROCEDURE

With the chamber pumped down to its base operating pressure (10^{-8} torr), the refrigeration He was cycled through the cryosphere. The temperature was monitored by the H₂ vapor pressure thermometer in the sphere, and the inlet and outlet temperatures at the refrigerator were also recorded. By adjusting the bypass valve at the refrigerator, the cryosphere was stabilized at the required temperature. The temperature as recorded by the vapor pressure thermometer in the cryosphere agreed within 1°K of the mean of the input-output temperatures at the cryostat.

Following the procedure outlined in Section IV, the mass spectrometer and ion gage were calibrated for H₂ by flowing gas into the chamber through a previously measured leak.

After calibration, the H₂ flow was stopped and the chamber pumped to its base pressure (approximately 5×10^{-9} torr). At this point, the diffusion pump was valved off and the CO₂ admitted to the chamber through its gas addition system to precoat the sphere. The thin layers of CO₂ were formed by adding CO₂ to the chamber for a known time while a constant forepressure was maintained on the calibrated leak. Since it would have taken an excessively long time to use this same method for forming the thicker layers, the following technique was used. The CO₂ was bled into the surge tank to raise the pressure to the 300-mm range; then the surge tank system was closed, and the pressure recorded. The valve to the chamber was then slightly opened, and the pressure drop in the surge tank monitored. Chamber pressures below 50 μ were maintained during these additions. When the surge tank pressure had dropped to the desired level, the valve to the chamber was closed. From the volume of the surge tank system, the initial and final pressure, the total quantity of CO₂ admitted was calculated. The heat load from this gas addition caused a slight rise in the cryosphere temperature. The total cryodeposit was cooled to the required test temperature after the gas flow was shut off.

The H₂ was admitted to the chamber through its gas addition system for a measured interval and then shut off. A record of the resulting pressure rise and drop was made from the mass spectrometer trace. The additions of H₂ were repeated until the partial pressure of H₂ rose too high to be further monitored by the mass spectrometer. For the thicker deposits of CO₂, the H₂ was added at higher rates so that the CO₂ could be saturated in the time available.

The following tests were made since anticipated user tests would require a pump capable of removing a mixture of H₂ and N₂, and Busol et al. had reported that N₂ cryodeposits would not sorb H₂ (Ref. 4). The sphere was precoated with CO₂, and the chamber was then valved closed. The CO₂ gas addition system was pumped out and flushed with N₂. Hydrogen was then admitted to the chamber via a known leak and the pumping speed of the CO₂ cryodeposit recorded by noting the equilibrium H₂ partial pressure. The valve to the N₂ system was opened and N₂ admitted simultaneously.

The H₂ pumping speed of the CO₂ cryodeposit immediately started to deteriorate as evidenced by the slow rise in H₂ partial pressure. The N₂ flow was interrupted, and again the H₂ equilibrium partial pressure was recorded.

This procedure was repeated for several different N₂ flow rates. Each successive N₂ addition caused a decrease in the H₂ pumping speed of the CO₂ cryodeposit.

SECTION IV CALIBRATION

4.1 LEAKS

Each leak was calibrated for the gases used, by recording the pressure drop in a known volume, as the gas flowed from this volume through the leak into the vacuum chamber (Ref. 2). Consider two volumes at pressures P_f and P_c, respectively, connected by a small leak with a conductance k. The resulting gas flow through the leak may be expressed as

$$V_f \frac{dP_f}{dt} = k (P_f - P_c)$$

If the pressure P_c is kept much lower than P_f by a pumping system, then the expression may be written

$$V_f \frac{dP_f}{dt} = k P_f$$

and

$$\frac{dP_f}{P_f} = \frac{k}{V_f} dt$$

Integration yields

$$\ln P_f = \frac{k}{V_f} t + \ln C$$

Using the initial conditions, $t = 0$, $P_f = P_i$. Then

$$\ln \frac{P_f}{P_i} = \frac{kt}{V_f}$$

Thus, the conductance of the leak is given by

$$k = \frac{V_f}{t} \ln \frac{P_f}{P_i}$$

The known volume, V_f , was measured by filling the components of the system with alcohol and measuring each volume during assembly. The pressure-time response during calibration was measured with a calibrated pressure transducer.

4.2 PUMP ORIFICE AND GAGE CALIBRATION

The vacuum system was pumped down with the diffusion pump, and the shroud was cooled to 77°K. The base pressure was measured by the ion gages. The pump was then closed off with the 6-in. gate valve, and the rate of rise caused by outgassing was recorded.

Using the previously calibrated leak, H_2 was admitted to the chamber at a known rate. With the gate valve open, the H_2 was pumped from the chamber via the orifice, and the steady-state pressures from both ion gages were recorded. The gate valve was then closed, and the rate of rise of the pressure in the chamber for this same in-flow rate was noted. This procedure was repeated with increasing H_2 flows until all scale ranges of the ion gages had been covered, with at least three data points on each scale.

The accumulated data were used in the following analysis to determine the gage sensitivity factors and the conductance of the orifice. Although the conductance of the orifice could be calculated, it was also measured experimentally to check the consistency of the equations, the applicability of kinetic theory, and the gage calibrations. The calculated value of the H_2 conductance using the Clausing factor (Ref. 7) was 141.5 l/sec. The experimentally determined value was 143 l/sec with a scatter of less than 5 percent. This agreement indicates that the experimental error in calibration does not exceed 5 percent.

4.2.1 Gage Calibration (Ion Gages)

From the ideal gas law

$$P \frac{dV}{dt} + V \frac{dP}{dt} = \frac{dn}{dt} RT$$

The gas flowing into the chamber may be considered as the sum of that through the leak Q_1 plus an outgassing load. Therefore,

$$P \frac{dV}{dt} + V \frac{dP}{dt} = Q_1 + \xi \tag{1}$$

With the main gate valve closed, $\frac{dV}{dt} = 0$ and

$$\frac{dP}{dt} = \frac{Q_1 + \xi}{V}$$

Assuming a constant outgassing rate it can be shown that

$$\sigma_{on} \dot{P}_{on} = \sigma_{cn} \dot{P}_{cn} = \frac{P_f k + \xi}{V} \tag{2}$$

where subscript cn refers to the c gage on the n scale and on refers to the o gage on the n scale.

Thus,

$$\frac{\dot{P}_{on}}{\dot{P}_{cn}} = \frac{\sigma_{cn}}{\sigma_{on}} \tag{3}$$

and a ratio of gage factors is obtained. From Eq. (2)

$$\dot{P}_{cn} = \frac{k}{\sigma_{cn} V} P_f + \frac{\xi}{\sigma_{cn} V} \tag{4}$$

Therefore, plotting \dot{P}_{cn} versus P_f yields a straight line when outgassing is either constant or negligible. The volume V was determined during assembly of the chamber by measuring components and calculating the resultant volume. The values of σ_{cn} were determined by the slope of the straight line from Eq. (4), and σ_{on} was calculated from Eq. (3).

4.2.2 Orifice Calibration

Determination of the conductance of the orifice was made using the steady-state pressures. Since $\frac{dp}{dt} = 0$, then Eq. (1) reduces to

$$P \frac{dV}{dt} = Q_1 + \xi \tag{5}$$

For this chamber, at the higher leak rates, $\xi \ll Q_1$, so that the outgassing may be ignored during calibration of the orifice. Thus,

$$P_c K - P_o K = P_f k$$

where K is the orifice conductance

and

$$K = \frac{P_f k}{P_c - P_o}$$

Using the calibration factors already determined for the gages,

$$K = \frac{P_f k}{\sigma_{cn} P_{cn} - \sigma_{on} P_{on}}$$

Rewriting this expressing

$$K = \frac{P_f k}{\sigma_{cn} P_{cn} \left(1 - \frac{\sigma_{on} P_{on}}{\sigma_{cn} P_{cn}}\right)}$$

Over the range of flow rates used in these experiments, the ratio $\frac{\sigma_{on} \rho_{on}}{\sigma_{cn} \rho_{cn}}$ was found to be a constant. Therefore, we may define a K effective as

$$K_{eff} = K \left(1 - \frac{\sigma_{on} P_{on}}{\sigma_{cn} P_{cn}}\right) = \frac{P_f k}{\sigma_{cn} P_{cn}}$$

4.2.3 Calibration of Mass Spectrometer

The mass spectrometer was tested for linearity by closing off the diffusion pump and admitting H₂ to the chamber at a known rate. The resulting rate of rise of pressure as recorded by the mass spectrometer was linear over the pressure range to be used in these experiments (10⁻⁸ to 10⁻⁵ torr). The mass spectrometer was calibrated by flowing the H₂ into the chamber at a known rate with the diffusion pumping system removing the gas through the orifice. A record of the flow rates was plotted versus the equilibrium chamber pressures as recorded by the mass spectrometer. These data were obtained before each experimental run and constituted the calibration for the mass spectrometer.

4.2.4 Calculation of Pumping Speeds

Since the effective conductance of the orifice was known, it was not necessary to calculate a gage factor per se for the mass spectrometer in order to calculate pumping speeds of the cryodeposit. During the calibration, we may express the equilibrium conditions as:

$$P_{f_1} k_1 = \sigma_{ms} P_{ms_1} K_{eff}$$

Whereas during the pumping runs made with the diffusion pump valved off, the equilibrium condition may be written as

$$P_{f_2} k_2 = \sigma_{ms} P_{ms_2} S$$

where S is the pumping speed of the cryodeposit.

Therefore,

$$\frac{P_{f_1} k_1}{P_{f_2} k_2} = \frac{\sigma_{ms} P_{ms_1} K_{eff}}{\sigma_{ms} P_{ms_2} S}$$

and

$$S = \frac{P_{ms_1}}{P_{f_1}} \cdot \frac{P_{f_2}}{P_{ms_2}} \cdot \frac{k_2 K_{eff}}{k_1}$$

SECTION V RESULTS

The H₂ partial pressure was monitored with a magnetic deflection-type mass spectrometer. This particular instrument is capable of reading partial pressures on the order of 5 x 10⁻¹⁰ torr. However, with no H₂ being admitted to the chamber, a H₂ background peak of 5 x 10⁻⁸ torr was observed. This peak was insensitive to pumping changes from 143 l/sec (calibration orifice) to 28,000 l/sec (12°K CO₂ cryodeposit) in the chamber. In calibrating the instrument, this background shows up as a zero shift in an otherwise linear calibration. It was, therefore, assumed that if this base peak represented a true H₂ gas partial pressure, it was being produced in the mass spectrometer head itself. The cell pressure was monitored by a Bayard-Alpert-type ion gage which indicated a pressure of 2 x 10⁻⁹ torr in the test chamber. Because of this masking effect of the actual base pressure in the cell, the "capacity" of a particular CO₂ cryodeposit was chosen as the quantity of H₂ required to raise the chamber partial pressure above 5 x 10⁻⁷ torr and thus be readily observable by the mass spectrometer. This definition is somewhat arbitrary but is necessary to allow us to compare the effects of temperature and thickness upon the pumping ability of the cryodeposit.

5.1 EFFECTS OF CRYODEPOSIT THICKNESS

The experimental results are divided into two groups: thin and thick deposits.

5.1.1 Thin Deposits

These deposits consisted of about 30 torr-ℓ of CO₂ which, assuming the bulk density of the cryodeposit as 1.5 gm/cc, represents a 5×10^{-5} cm layer. In each case, these deposits were made after the surface had reached the operating temperature chosen for the particular test run. At no time did the cell pressure rise above 10^{-4} torr during deposition of the cryolayer.

5.1.2 Thick Deposits

These deposits consisted of about 500 torr-ℓ of CO₂ which represents a layer about 1 μ thick. The thickness of the CO₂ cryodeposit had no noticeable effect on the initial pumping speed of the H₂ at any of the temperatures tested. The capacity of the cryodeposit, however, seems to be a direct function of the quantity of the deposit over the range of thicknesses investigated (Fig. 3). Several deposits of CO₂ were left for periods of up to 1 hr before pumping runs were made to see if any tempering effects were noticeable, but none were found.

5.2 EFFECTS OF THE TEMPERATURE OF THE CRYODEPOSIT

Three temperatures were chosen for investigation: 20, 16, and 12°K. The radiation load in all cases, except one, was 300°K. The one result with a 77°K radiation load is noted separately. No pumping was observed for a cryodeposit at 25°K.

As can be seen in Table I, the most notable effect of the temperature is reflected in the capacity of the cryodeposit. A plot of the ratio of CO₂

TABLE I
RATIO OF CO₂/H₂ FOR VARIOUS TEMPERATURES

Temperature of Cryodeposit, °K	Amount CO ₂ Deposited, torr-ℓ	Amount H ₂ to Reach "Capacity", torr-ℓ	Ratio CO ₂ /H ₂	
20	30.3	0.06	500	
	30.3	0.10	300	
	630.0	2.04	309	
16	30	0.63	47.5	
	30	0.63	47.5	
	514	9.0	57.0	
12	30	3.75	8.0	
	40	5.05	7.9	
	495	58.0	8.5	
for 20°K cryodeposit and 77°K shroud		495	9.0	55.0

to H₂ versus temperature (Fig. 4) indicates the order of magnitude improvement in the capacity as the temperature is lowered. The pumping speed of the cryodeposit shows some improvement with decreasing temperature. Average pumping speeds for 300°K H₂ were 14 l/sec-cm² for 20°K cryodeposits, 19 l/sec-cm² for 16°K cryodeposits, and 28 l/sec-cm² for 12°K cryodeposits. These values are for H₂ addition rates on the order of 1 x 10⁻³ torr-l/sec with H₂ partial pressures in the 10⁻⁸ torr range. A pressure dependence of the pumping speed as reported by Busol et al. (Ref. 4) was confirmed for the 20°K cryodeposits (Table II).

TABLE II
PUMPING SPEED OF H₂ VERSUS TEMPERATURE OF CO₂

Temperature of Deposit, °K	Flow Rate of H ₂ , torr-l/sec	H ₂ Partial Pressure during Pumping, torr	Pumping Speed, l/sec-cm ²
Data taken September 23, 1966			
12.0	1.0 x 10 ⁻³	3.52 x 10 ⁻⁸	28.6
	6.0 x 10 ⁻³	2.14 x 10 ⁻⁷	28.4
	1.2 x 10 ⁻²	4.32 x 10 ⁻⁷	28.2
	3.5 x 10 ⁻²	1.27 x 10 ⁻⁶	27.9
	7.05 x 10 ⁻²	2.51 x 10 ⁻⁶	28.3
	1.06 x 10 ⁻¹	3.82 x 10 ⁻⁶	28.1
	1.42 x 10 ⁻¹	5.1 x 10 ⁻⁶	28.2
Data taken October 3, 1966			
16.0	1.0 x 10 ⁻³	5.27 x 10 ⁻⁸	19.2
	2.0 x 10 ⁻³	1.11 x 10 ⁻⁷	18.2
	6.0 x 10 ⁻³	3.30 x 10 ⁻⁷	18.4
	1.2 x 10 ⁻²	7.81 x 10 ⁻⁷	16.5
	2.0 x 10 ⁻²	1.42 x 10 ⁻⁶	14.3
Data taken September 22, 1966			
20.0	1.0 x 10 ⁻³	6.95 x 10 ⁻⁸	14.6
	2.0 x 10 ⁻³	1.48 x 10 ⁻⁷	13.7
	6.0 x 10 ⁻³	1.44 x 10 ⁻⁶	4.2
	1.2 x 10 ⁻²	3.75 x 10 ⁻⁶	3.2
	2.0 x 10 ⁻²	8.4 x 10 ⁻⁵	0.24
Data taken October 4, 1966 (Pressure and Pumping Speed Converted to 300°K)			
20.0 (77°K Shroud)	1.0 x 10 ⁻³	3.12 x 10 ⁻⁸	31.8
	2.0 x 10 ⁻³	7.62 x 10 ⁻⁸	26.6
	6.0 x 10 ⁻³	3.24 x 10 ⁻⁷	18.4
	1.2 x 10 ⁻²	7.3 x 10 ⁻⁶	16.4
	2.0 x 10 ⁻²	1.26 x 10 ⁻⁶	15.6

For these deposits, as the H₂ inflow was increased, the pumping speed started to deteriorate. However, if the H₂ flow was interrupted and then

restarted after the H₂ partial pressure had dropped to its base level, the pumping speed recovered for a short time before again starting to deteriorate.

For the 16°K cryodeposits, this deterioration of the pumping speed was not so pronounced, and recovery after an interruption was much faster. With the 12°K cryodeposits, no deterioration in pumping speed for H₂ flows up to 0.14 torr-ℓ/sec (H₂ partial pressure of 5×10^{-6} torr) was noted. A summary of pumping speed versus H₂ partial pressure is shown in Fig. 5.

The 20°K cryodeposit, surrounded by a 77°K radiation shield, showed a marked increase in initial pumping speed. However, the shape of a plot of the deterioration of pumping speed of this deposit versus H₂ partial pressure shows a marked resemblance to that of the 20°K cryodeposit with 300°K radiation (Fig. 5).

5.3 CONTAMINATION OF CRYODEPOSIT BY N₂

In this test, 495 torr-ℓ of CO₂ were predeposited and cooled to 12°K. Hydrogen was admitted to the cell at a flow rate of 2.1×10^{-2} torr-ℓ/sec. The initial pumping speed was 28.0 ℓ/sec-cm² which agrees with previous runs. Figure 6 shows a plot of the H₂ partial pressure as indicated by the mass spectrometer versus time as N₂ was admitted at different rates. Previous pumping runs with this thickness cryodeposit and the same H₂ inbleed rate showed no deterioration in pumping speed over a similar time period. A plot of pumping speed/cm² versus N₂ added/cm² pumping surface indicates a near logarithmic dependence as indicated in Fig. 7. A plot of rate of deterioration in pumping speed versus rate of N₂ addition is shown in Fig. 8 indicating a linear relationship.

SECTION VI DISCUSSION

The data reported from these investigations cover a wide range of variables, and although no specific answers may be given from such a survey, several suggestions may be made concerning the mechanics of H₂ sorption by the cryodeposits. From the variation of thickness data, it would seem that within the range of these tests the complete cryodeposit is active in the sorption process at all the temperatures. An analysis of the pumping by different temperature cryodeposits indicates that the sorption process might be considered in two parts:

1. Impingement of H₂ molecules at the surface of the cryodeposit results in surface capture. For a fixed quantity of H₂ added to

the system, one would thus expect an equilibrium to be established where for a specific concentration of H₂ molecules within this surface, the re-evaporation rate would match the condensation rate. At this point the pumping would stop. However, coupled with this process there is:

2. A diffusion of H₂ molecules within the cryodeposit matrix from the region of high concentration at the surface. The rate constant for this diffusion is evidently strongly dependent upon the cryodeposit temperature.

This model will explain the pressure dependence of the pumping speed measurements made on 20°K cryodeposits and account for the recovery in pumping speed after a brief pause in H₂ additions. Also, the data presented in Fig. 5 for the pumping speed of a 20°K deposit with a 77°K shroud indicate that whereas the surface capture is improved by reducing the radiation load, the pumping speed is still limited by the inability of the H₂ molecules to diffuse into the cryodeposit matrix quickly enough.

It might be noted that the data presented in Fig. 5 should be accepted as indicating a trend rather than presenting absolute values. Since there is a correlation between the pumping speed at the surface and the relative saturation of the substrate, absolute values should be taken with a fresh cryodeposit for each data point. Although different cryodeposits were used for each temperature range shown in these data, pumping speed measurements were made in succession as the H₂ inflow rate was increased stepwise. These cryodeposits were above 1 μ thick. However, using thick layers of CO₂ reduces but does not eliminate the effect of H₂ sorbed in determining the previous data point.

An apparent logarithmic dependence of the ratio of quantities of CO₂ predeposited to H₂ required to saturate to capacity versus temperature is shown in Fig. 4. The limited scatter of these data warrants a more refined investigation of the effects of the cryodeposit's capacity as a function of its temperature. Investigation over a wider range of cryodeposit thicknesses at intermediate temperatures would help to better define this relationship.

The pumping speeds indicated in Fig. 7 show the adverse effects of N₂ condensing on the CO₂. The rapid equilibrium established when the N₂ flow was interrupted (as shown in Fig. 6) would indicate that the N₂ is confined to the surface rather than diffusing into the cryodeposit. A near logarithmic dependence between pumping speed and quantity of N₂ deposited was not expected. The data thus indicate that the poisoning does

not consist of a simple blocking of condensation sites, but rather acts as a permeable barrier. One would expect that with increasing thickness of this barrier, there would be a gradual transition from the pumping speed of H₂ on CO₂ cryodeposit to that of H₂ on N₂ cryodeposit.

SECTION VII SUMMARY

Carbon dioxide cryodeposits may be used as an effective method of cryopumping H₂. The 12°K cryodeposits yielded pumping speeds of 28 l/sec-cm² with no pressure dependence up to 5 x 10⁻⁶ torr. The 16°K cryodeposits yielded pumping speeds of 19 l/sec-cm² with a drop in pumping speed at pressures above 5 x 10⁻⁷ torr, and 20°K cryodeposits yielded pumping speeds of 14 l/sec-cm² with a drop in pumping speed at pressures above 5 x 10⁻⁸ torr.

The capacity of the cryodeposits is a direct function of its thickness within the range investigated and increases logarithmically as its temperature is lowered.

No pumping was observed with the cryodeposit above 25°K.

The cryodeposit is readily contaminated with N₂, and use of this system to pump mixtures of N₂ and H₂ would require shielding by 20°K baffles to remove the N₂ before it reached the CO₂ surface. Such shields would also reduce the radiation load and thus improve the pumping speed of the cryodeposit; however, this gain might be offset by losses caused by the limiting conductance of the baffle.

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**APPENDIX
ILLUSTRATIONS**

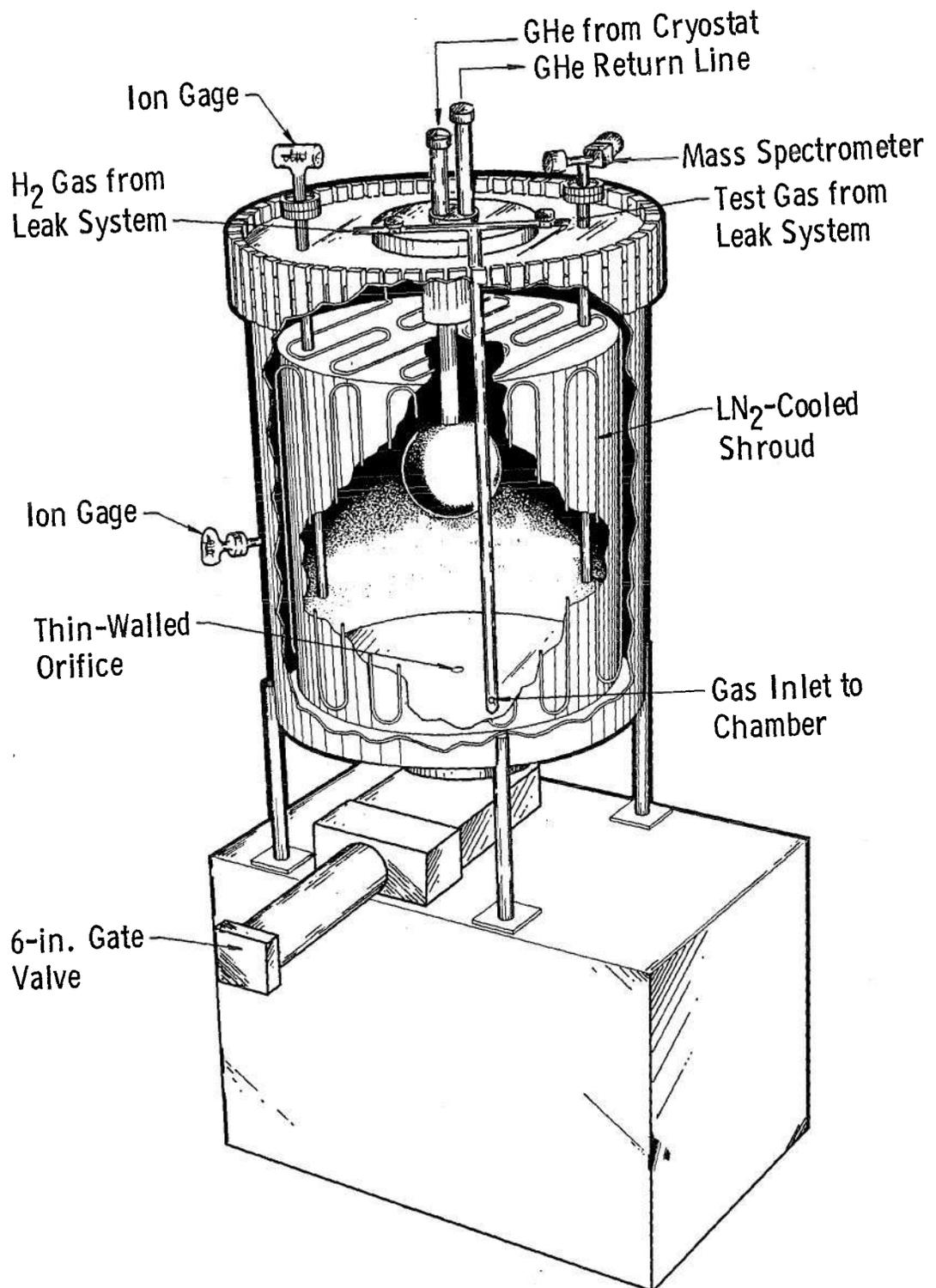


Fig. 1 UHV Chamber

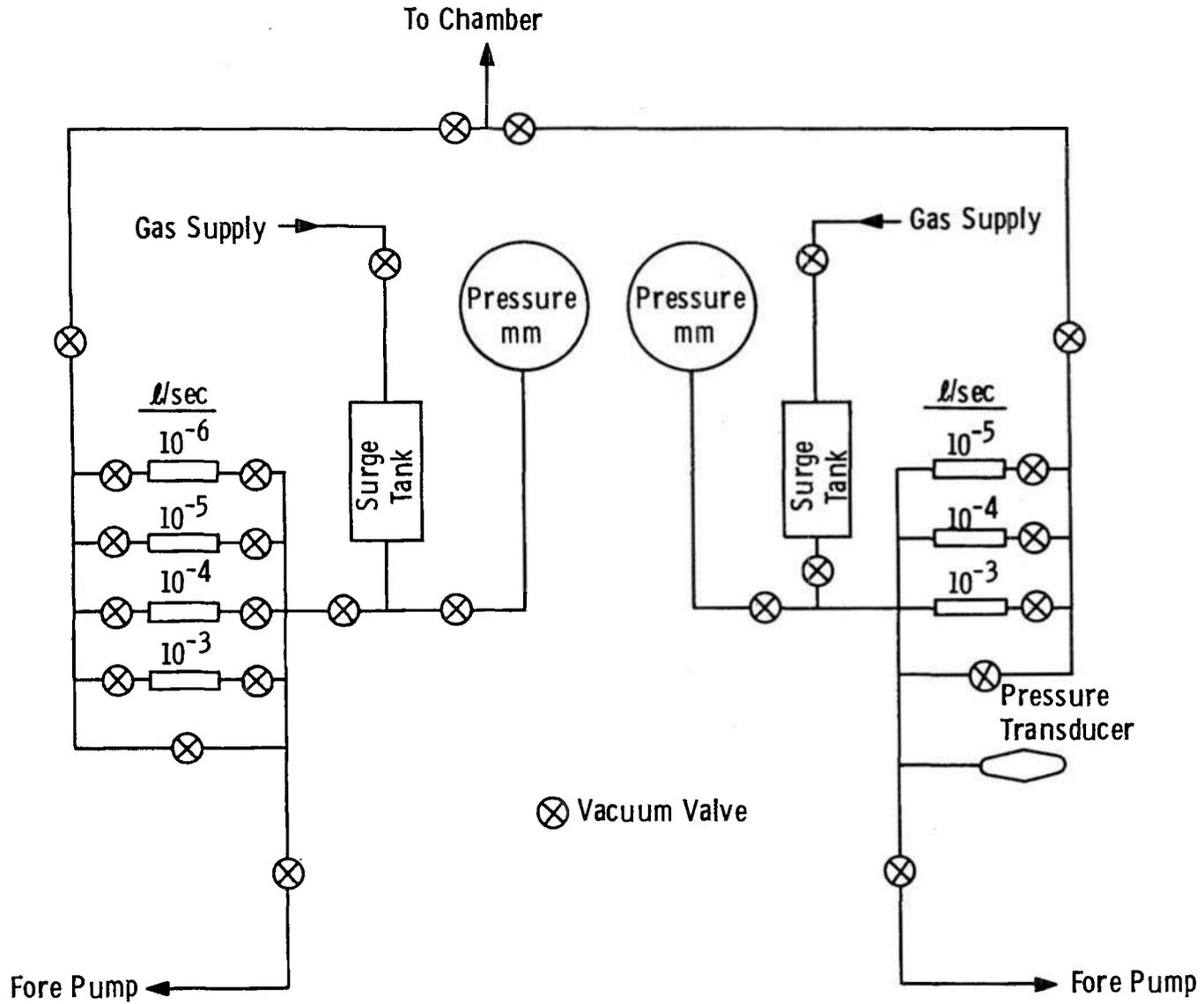


Fig. 2 Gas Addition System

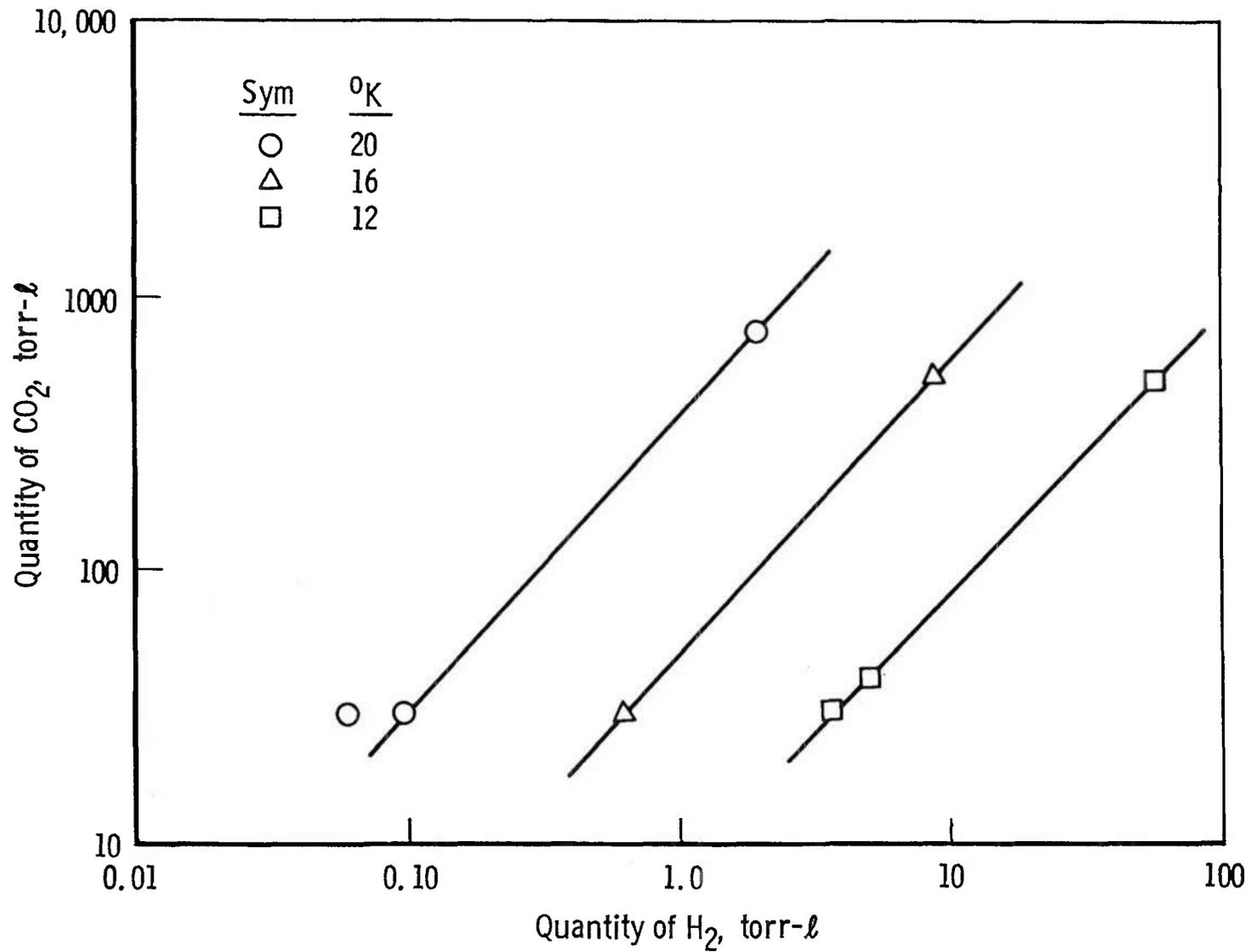


Fig. 3 Quantity of CO₂ Added versus H₂ Required to Reach Capacity

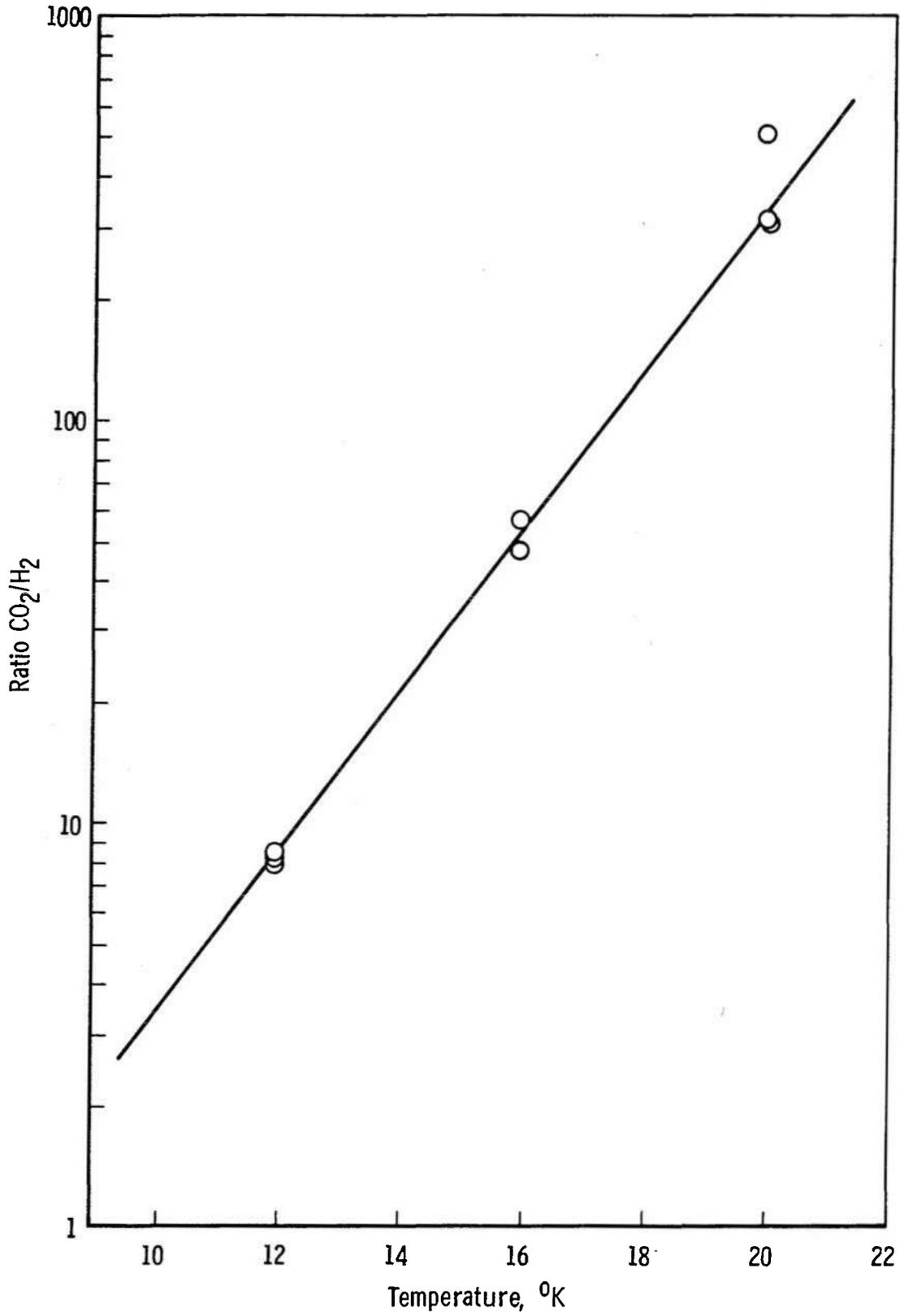


Fig. 4 Ratio of CO₂/H₂ (from Fig. 3) Plotted against Temperature

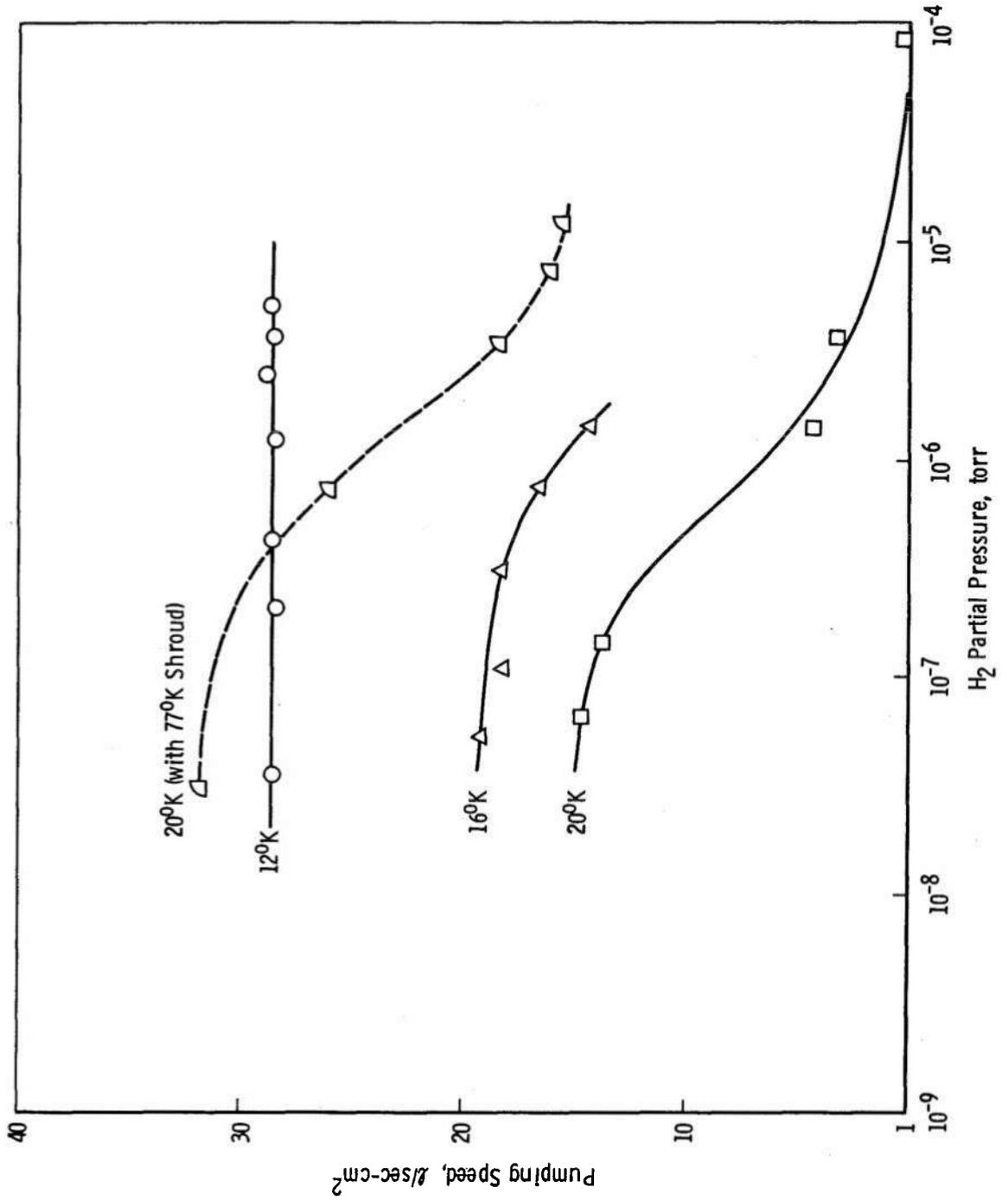


Fig. 5 Pressure Dependence of Pumping Speed

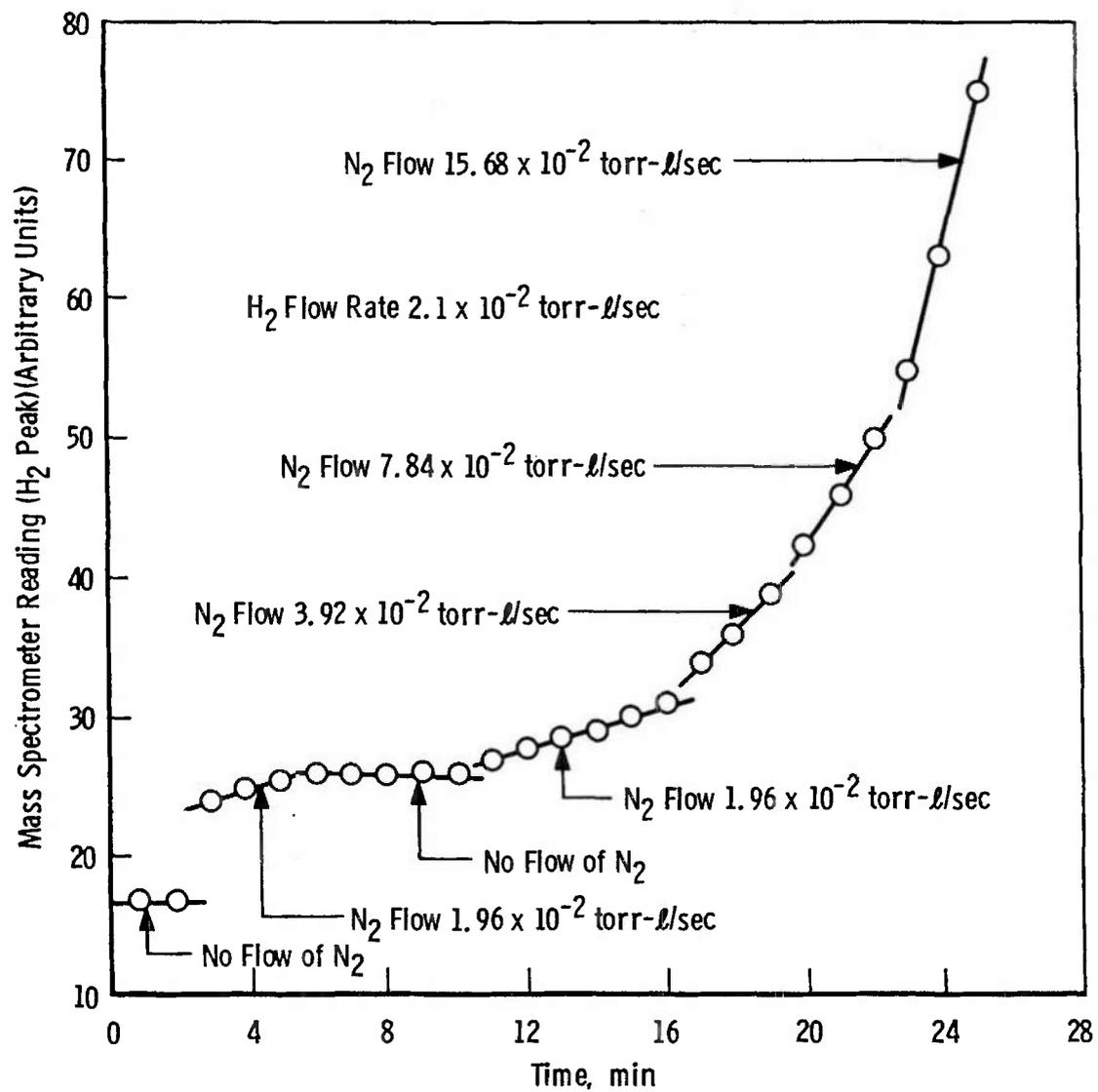


Fig. 6 Mass Spectrometer Trace during Poisoning of CO₂ Surface by N₂

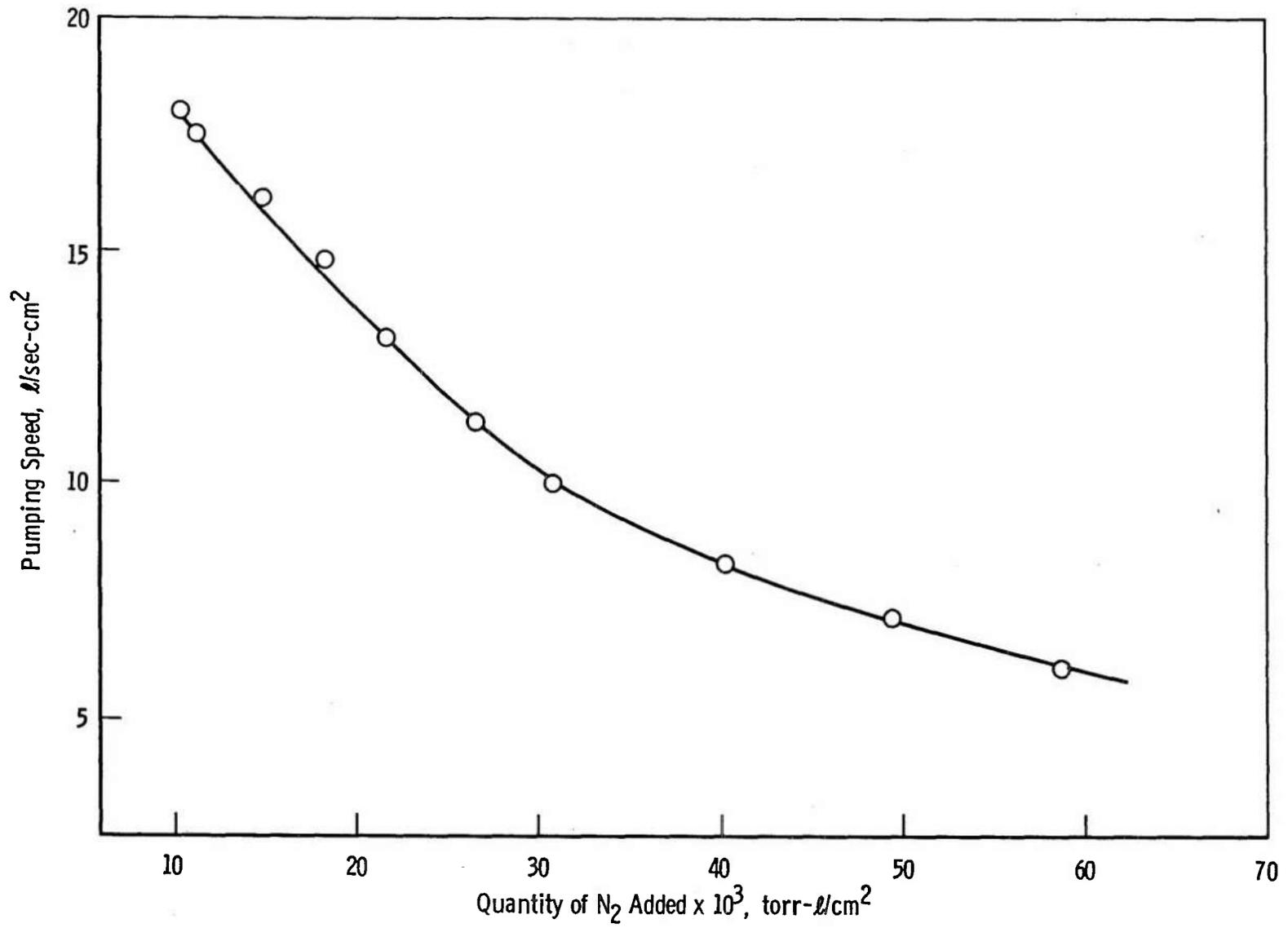


Fig. 7 Pumping Speed of Cryodeposit during Poisoning

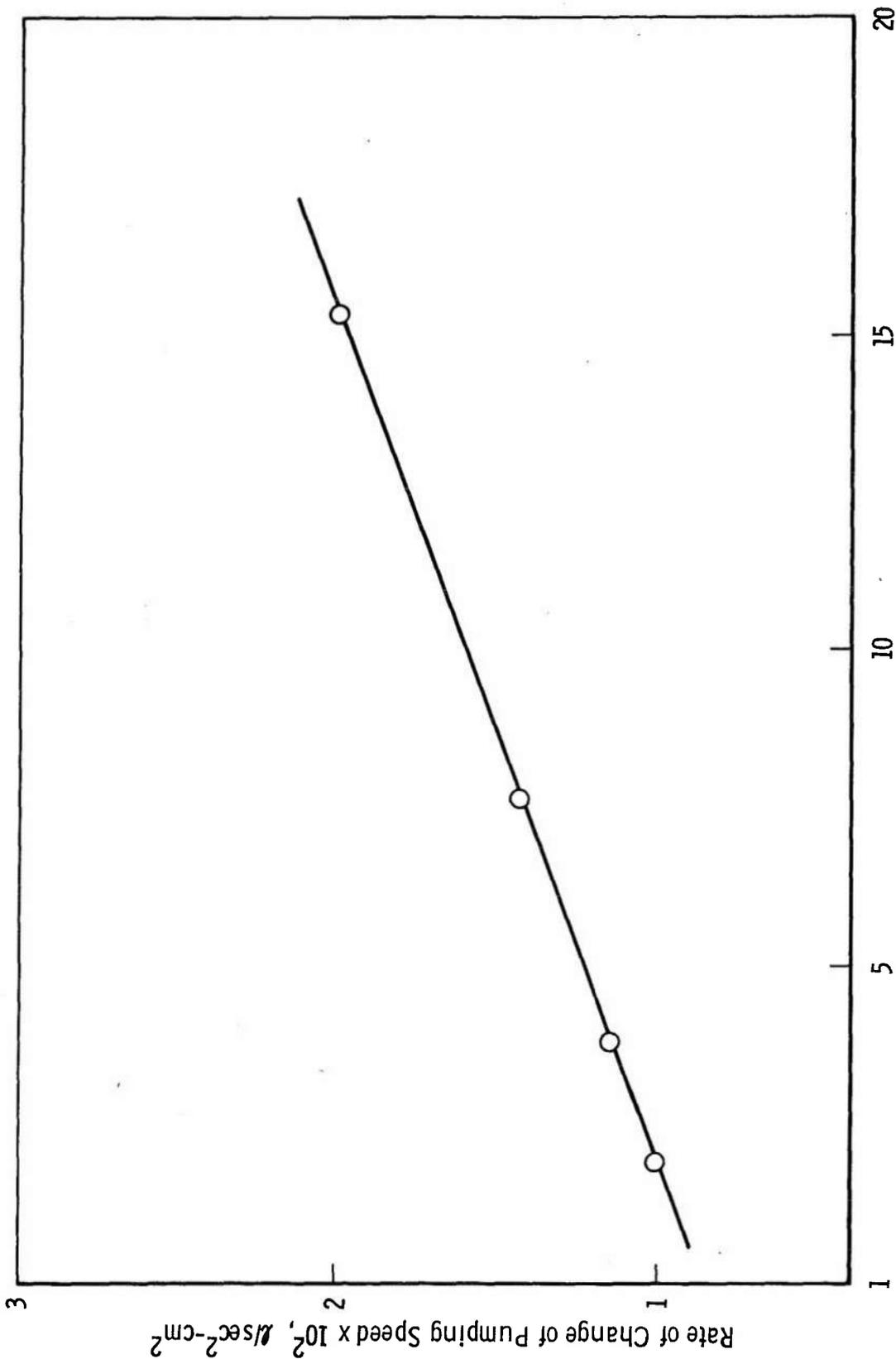


Fig. 8 Rate of Deterioration of Pumping Speed versus Rate of N_2 Addition

DOCUMENT CONTROL DATA - R&D

(Security classification of title, body of abstract and indexing annotation must be entered when the overall report is classified)

1. ORIGINATING ACTIVITY (Corporate author) Arnold Engineering Development Center ARO, Inc., Operating Contractor Arnold Air Force Station, Tennessee		2 a. REPORT SECURITY CLASSIFICATION UNCLASSIFIED	
		2 b. GROUP N/A	
3. REPORT TITLE CRYOSORPTION OF HYDROGEN BY 12-20°K CARBON DIOXIDE CRYODEPOSITS			
4. DESCRIPTIVE NOTES (Type of report and inclusive dates) Final Report September to October 1966			
5. AUTHOR(S) (Last name, first name, initial) R. Dawbarn, ARO, Inc.			
6. REPORT DATE July 1967	7 a. TOTAL NO. OF PAGES 30	7 b. NO. OF REFS 7	
8 a. CONTRACT OR GRANT NO. AF 40(600)-1200	9 a. ORIGINATOR'S REPORT NUMBER(S) AEDC-TR-67-125		
b. PROJECT NO.	9 b. OTHER REPORT NO(S) (Any other numbers that may be assigned this report)		
c. Program Element 65402234	N/A		
d.			
10. AVAILABILITY/LIMITATION NOTICES This document has been approved for public release and sale; its distribution is unlimited.			
11. SUPPLEMENTARY NOTES Available in DDC		12. SPONSORING MILITARY ACTIVITY Arnold Engineering Development Center Air Force Systems Command Arnold Air Force Station, Tennessee	
13. ABSTRACT Carbon dioxide cryodeposits were investigated to determine their ability to sorb H ₂ . Various thickness from 5 x 10 ⁻⁵ to 1 x 10 ⁻³ cm were used, at temperatures of 12, 16, and 20°K. Pumping speeds of 28, 19, and 14 l/sec-cm ² were measured for the respective temperatures. An arbitrary "Capacity" of the CO ₂ cryodeposit for H ₂ was defined. Within the limits of the experimental parameters varied, this capacity was found to be a direct function of the thickness of the cryodeposit and increased logarithmically as the temperature was lowered. No cryopumping of H ₂ was observed with cryodeposits above 25°K. The CO ₂ cryodeposits were readily contaminated by N ₂ , and the H ₂ pumping speed dropped when N ₂ was flowed in simultaneously with the H ₂ .			

14. KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT
1 cryosorption hydrogen 2 carbon dioxide cryodeposits 3 "						
3, Hydrogen -- sorption						
15-2						